

I. ATOMIC WEIGHT OF TUNGSTEN.  
II. AMMONIUM TUNGSTATES.

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THESIS

Presented to the Faculty of the Department of Philosophy  
of the  
University of Pennsylvania  
In Partial Fulfillment of the Requirements  
for the  
Degree of Doctor of Philosophy

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### ACKNOWLEDGMENT.

This study was prosecuted under the direction of Professor Edgar F. Smith. It is only with appreciation of the privilege of working under his direction, that I offer my thanks, to him whose love for chemistry is an inspiration and whose kindness that of a father.

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## INTRODUCTION.

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The object in mind when the present investigation was undertaken, was not primarily the establishment of the atomic weight of tungsten. It was rather to ascertain by working up unusually large quantities of "starting-out material" to discover whether there were not present minute quantities of other elements, which accompanied the tungsten through its many compounds, and escaped recognition in the numerous efforts put forth to get a pure product. These experiments have brought to light the facts which are detailed in Part I. They constitute a definite contribution to our knowledge of disturbing factors in the determination of this particular constant.

The ammonium tungstates as described in Part II., show interesting relationships. The suggestions as to constitution are instructive, but can only be adopted after we possess, definite experimental evidence as to the molecular weights of these compounds. The existence of the colloidal ammonium salt is rather in the nature of a surprise, although its frequent reproduction and the concordant analyses prove its individuality, and that it is not a chance product. The manner in which water is substituted for ammonia and *visa versa*, recalls the deportment of salts of copper in the same direction, and gives additional confirmatory evidence of this behavior of hydrated and ammoniated bodies.



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## I. ATOMIC WEIGHT OF TUNGSTEN.

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The wide variability in the atomic weight determinations of tungsten, suggest that there is some impurity, or possibly some closely associated element, which clings tenaciously to tungsten and its derivatives. With a view of searching for this disturbing factor, and of finding a more accurate method than those hitherto used, the following study was undertaken.

The material used had been extracted from 11.34 kilograms of Wolframite from Conn., and had undergone the following treatment:

1st. Tungsten trioxide was separated from Wolframite by *aqua regia*, and washed with acidulated water.

2nd. This oxide was dissolved in distilled ammonia.

3rd. The ammonium tungstate was crystallized, and the first fraction collected, which being deposited from a large bulk of water was unusually white.

4th. This fraction was redissolved in water and ammonia, and again crystallized, and the first fraction preserved.

5th. This perfectly white salt was ignited in porcelain crucibles to bright "canary yellow" tungsten trioxide. Oftentimes on long ignition, a faint blush of red was noticed on the surface of the yellow oxide.

The method of reduction and oxidation has been the one most generally used, and to test the method the following experiments were made: A portion of the trioxide was placed in a porcelain boat, and reduced in hydrogen, using a thin walled porcelain combustion tube, glazed inside and out. The apparatus for generating and purifying the

hydrogen was the same as that used by <sup>(1)</sup>Hardin, and worked satisfactorily. The porcelain tube was heated directly with free flames, to the highest heat obtainable in a combustion furnace.

The weighings in these experiments were made on a Troemner short arm balance, sensitive to the fortieth of a milligram, supplied with calibrated weights. No reductions to a vacuum standard were made.

#### Reduction No. 1.

	Time Hours	Weight of WO <sub>3</sub> grams	Weight of W grams	Atomic Weight of Tungsten
(1)	3	1.74898	1.38611	183.35
(2)	6	1.74898	1.38589	183.21
(3)	9	1.74898	1.38587	183.20

The material was not removed from the boat during these reductions. As the time of heating progressed the atomic weight became lower, and after nine hours it did not become constant. The experiment was repeated with another sample:

#### Reduction No. 2.

	Time Hours	Weight of WO <sub>3</sub> grams	Weight of W grams	Atomic Weight of Tungsten
(1)	4	1.20096	0.95214	183.67
(2)	7	1.20096	0.95203	183.57
(3)	11	1.20096	0.95182	183.38
(4)	14	1.20096	0.95174	183.30
(5)	18	1.20096	0.95141	183.00
(6)	22	1.20096	0.95134	182.93

Constant weight was not obtained after heating for twenty-two hours.

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<sup>(1)</sup>*J. Am. Ch. Soc.*, **19**, 657. (1897).

## Reduction No. 3.

	Time Hours	Weight of $\text{WO}_3$ grams	Weight of W grams	Atomic Weight of Tungsten
(1)	4	2.77973	2.20447	183.94
(2)	8	2.77973	2.20423	183.84

The metal from the twenty-two hour reduction was oxidized in a porcelain crucible, in an atmosphere of oxygen for one-half hour.

## Oxidation Experiment No. 1.

Time Hours	Weight of W grams	Weight of $\text{WO}_3$ grams	Atomic Weight of Tungsten
0.5	0.93574	1.17882	184.77

It is observed that the same metal, which on reduction gave values from 183.67 to 182.93, on oxidation gives 184.77. Another portion of tungsten trioxide was ignited over a single Bunsen burner in oxygen for three hours, and a loss noted.

## Oxidation Experiment No. 2.

Time Hours	Weight of $\text{WO}_3$ grams	Weight of $\text{WO}_3$ grams	Loss grams
3	2.99239	2.99175	0.00064

Another sample of tungsten trioxide (which had been prepared from the metal ignited in air), was ignited for one hour in oxygen, and a gain noticed. After further ignition in oxygen for one hour, a loss was observed.

## Oxidation Experiment No. 3.

Weight of $\text{WO}_3$ grams	Weight of $\text{WO}_3$ after one hour	Weight of $\text{WO}_3$ after two hours
1.57355	1.57449	1.57285

After the first hour it gained 0.00094 grams; after the next hour, it lost 0.00070 grams. The explanation is probably, that the tungsten trioxide used had not quite reached its maximum oxidation. When ignited in oxygen it was fully oxidized, and further ignition produced a loss. The current of oxygen used was extremely slow (bubble by bubble), so that mechanical sweeping out of the material could hardly have occurred.

The porcelain tube employed in these reductions was new. After use, it was swabbed with filter paper, which now showed dark spots. The porcelain boats were white, but after the reductions they were dark all over the outside, and even on the bottom. In some cases the porcelain boats were partly surrounded with platinum foil, and a deposit occurred on the porcelain in such a manner, that the position protected by the platinum foil was clearly marked on the outside of the boat, by being lighter in color. The platinum also was stained with a deposit. On oxidation the darkened sides of the boat became nearly white, so that the dark material was undoubtedly tungsten.

From a consideration of these results it appears, that with the material used, and by varying the conditions of reduction or oxidation, almost any figure could be obtained for the atomic weight of tungsten. How different determinations may be reduced or oxidized to a constant and comparable weight, is difficult to understand. It probably can only be done by making the conditions precisely alike in every determination. A requirement which at times may be misleading.

A few more determinations by this method were made, on the tungsten trioxide contained in colloidal ammonium tungstate. In this case the reductions were continued for three hours, and the oxidations for one hour in oxygen; and all determinations were made as nearly alike as possible, so that the results might be comparable.



## Reduction Series.

Material	Weight of $\text{WO}_3$ grams	Weight of W grams	Atomic Weight of Tungsten
(1) Dialyzed (13 days)	2.35730	1.86939	183.91
(2) Undialyzed	2.39381	1.89763	183.57
(3) First fraction	2.13506	1.68995	182.24

## Oxidation Series.

Material	Weight of W grams	Weight of $\text{WO}_3$ grams	Atomic Weight of Tungsten
(1) Dialyzed (13 days)	0.72938	0.91954	184.11
(2) Undialyzed	0.62988	0.79346	184.82
(3) First fraction	0.48514	0.61166	184.05

These results show, that the tungsten trioxide from the dialyzed salt, gives a higher atomic weight than the material passing through the parchment paper. The variation in the difference between the reduction and the oxidation values, for the three different portions, is marked. This difference for the dialyzed material, is 0.20; for the undialyzed, 1.25; and for the first fraction (that portion passing through in twelve hours), 1.81. These results therefore indicate that dialysis is removing some crystalloid from the material, and that this substance is responsible for the difference between the reduction and oxidation values.

The tungsten trioxide resulting from these determinations was dissolved by boiling in a solution of pure sodium carbonate, when a white flocculent residue remained. The dialyzed material contained the same residue, but in smaller amount. When dissolved in potassium hydroxide the residue was not so evident. On standing a few hours in sodium carbonate, this residue turned reddish brown. On treatment with hot concentrated hydrochloric acid, it (having been previously washed) broke down into tungstic acid,

and the filtrate contained the chlorides of iron and manganese. To confirm the presence of these impurities in the metal from the reductions, it was boiled with pure hydrochloric acid, and iron detected in the liquid. Moreover, this iron could not be entirely removed by boiling acid. To see if some of the original ammonium tungstate would reveal the presence of these impurities, it was dissolved in water, feebly acidulated with hydrochloric acid, and ammonium sulphocyanate added. No coloration was produced. Another portion of the solution, was boiled with hydrochloric acid, the tungstic acid precipitated, and now the filtrate easily showed the presence of iron.

This residue appears to be a tungstate of iron and manganese, which probably existed in the ammonium salt, as an ammonium-iron-manganese tungstate. <sup>(1)</sup>Laurent states, that the mother liquor from which ammonium tungstate has been crystallized contains such a salt. He ascribed to it the formula: <sup>(2)</sup> $[12(\text{NH}_4)_2\text{O}, 6 \text{MnO}, 2 \text{Fe}_2\text{O}_3, 3 \text{H}_2\text{O}, 45 \text{WO}_3, 81 \text{H}_2\text{O}]$ .

<sup>(3)</sup>Borch analyzed this salt with the following results:  $\text{WO}_3$  84.4%,  $(\text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3)$  4.6%,  $\text{NH}_3$  4.0%,  $\text{H}_2\text{O}$  7%. Laurent states that this complex salt is soluble in water and ammonia, and is peculiar, in that ordinary reagents do not show the presence of iron, manganese, or tungstic acid. Further, that the salt is only broken down, by prolonged boiling in acids or alkalis, and then the ingredients can be readily detected.

<sup>(4)</sup>Schneider recognized the presence of this salt in ammonium tungstate, and stated that after five or six recrystallizations, it could not be removed. Also that it could not be removed by the ammonium sulphide treatment, for slight

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<sup>(1)</sup>*J. prakt. Ch.*, 42, 126. (1847).

<sup>(2)</sup>*Comptes rendus.*, 31, 693. (1850).

<sup>(3)</sup>*J. prakt. Ch.*, 54, 254. (1851).

<sup>(4)</sup>*J. prakt. Ch.*, 50, 152. (1850).

amounts of the sulphides of iron and manganese, are soluble in the tungsten sulpho-salt. <sup>(1)</sup>Berzelius stated that the sulphides of tungsten, iron, and manganese, form a compound which is partly soluble in water. <sup>(2)</sup>Taggart and Smith have shown that manganese and tungstic acid can not be separated by yellow ammonium sulphide, nor by aqueous potassium carbonate; and suggest the necessity of fusion with an alkaline carbonate.

Schneider, to remove this complex salt, purified his material in the following way: Tungstic acid obtained from the sulpho-salt of tungsten, was boiled in *aqua regia*, and washed in acidulated water till free from iron. This was dissolved in dilute ammonia, and the solution precipitated by boiling hydrochloric acid, the resulting tungstic acid boiled in *aqua regia* and again washed. This oxide was again dissolved in ammonia and again precipitated. After reprecipitating three times in this manner, a tungsten trioxide was obtained free from iron. However, on dissolving the oxide in potassium hydroxide, a slight brown residue remained which had escaped all earlier tests. The small amount of this as he assumes, was not enough to affect the result of his work.

A portion of the material used in the previous experiments in this paper, was treated with this reprecipitation method. It was dissolved in ammonium hydroxide, precipitated by boiling in *aqua regia*, the resulting oxide washed. This moist precipitate (without ignition) was again dissolved in ammonia and reprecipitated. In this manner the material was reprecipitated four times. A portion of it was then dried, ignited, and dissolved in boiling sodium carbonate. The residue very materially diminished was still there, and particularly noticeable after standing a few hours. Another portion of

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<sup>(1)</sup>*Pogg. Ann.*, 8,279. (1826).

<sup>(2)</sup>*J. Am. Ph. Soc.*, 18,1053. (1896).

this substance apparently dissolved completely in boiling potassium hydroxide, but on standing twenty-four hours a slight deposit was observed. In no case was this deposit as large as that in the comparison tube of sodium carbonate; which would indicate that the residue is more soluble in potassium hydroxide, than in sodium carbonate. Schneider admits that his purest material, showed a trace of residue when dissolved in potassium hydroxide. Had he applied the sodium carbonate test, this residue would probably have appeared larger. In the recent repetition of his <sup>(1)</sup>work, he used material purified in precisely the same manner, (in fact some of the original material) with the exception of the treatment for the elimination of molybdic acid.

<sup>(2)</sup>Borch recognized this complex salt, and tried to remove it by fusion with potassium carbonate. However, this treatment introduces fixed alkali, which is difficult to remove.

Later investigators seem not to have appreciated the difficulty of removing this complex salt; for it crystallizes in part with the ammonium tungstate, and can scarcely be entirely removed by recrystallization. Ignition of the ammonium salt, and resolution in ammonium hydroxide will not eliminate it. Nor will ammonium sulphide remove it. In fact it seems likely that it has never been wholly extracted, from any previous material.

The purification by <sup>(3)</sup>Pennington and Smith, would not remove it, for though closely following the method outlined by Schneider, and adding to it the complete elimination of molybdenum; they omitted the final repeated precipitations with acid. The metal used by them had the specific gravity 18.64, which appears low. Had the metal been alloyed with platinum, its specific gravity would have been higher,

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<sup>(1)</sup>*J. prakt. Ch.*, **161**,288. (1896).

<sup>(2)</sup>*J. prakt. Ch.*, **54**,254. (1851).

<sup>(3)</sup>*Proc. Am. Philos. Soc.*, **33**,332. (1894).

but this metal gave no test for platinum. <sup>(1)</sup>Moissan prepared metallic tungsten in the electric furnace; which was soft, would not scratch glass, and could be easily filed and welded like iron; produced no effect on the magnetic needle, and examined spectroscopically, showed the presence of no foreign ingredients, other than faint lines for calcium. It fused with more difficulty than chromium or molybdenum, and gave the following analysis:

	Tungsten Per cent.	Carbon Per cent.	Gangue Per cent.
(1)	99.76	00.00	00.18
(2)	99.82	00.00	00.09
(3)	99.87	00.00	00.00

The specific gravity of this metal was 18.7, and the presence of gangue would have lowered the specific gravity, so that the true value is probably higher.

The process of purification employed by Hardin for tungsten, would not remove the complex salt.

A review of the original material used by previous workers, shows that Schneider, Marchand, Borch, Pennington and Smith, Desi, Shinn, and probably nearly all the others, used Wolframite as the "starting-out material". In some cases the source of material has not been stated. Waddel started with Scheelite, but abandoned it for commercial metal of unstated origin.

This complex salt, obviously can not come from Scheelite, which is essentially a calcium tungstate. Determinations with Scheelite material have been made by <sup>(2)</sup>Hardin, and <sup>(3)</sup>Thomas and Hardin. The results for the purpose of comparison are again presented:

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<sup>(1)</sup> *Comptes. rendus.*, 123, 13-16. (1896).

<sup>(2)</sup> *J. Am. Ch. Soc.*, 19, 657. (1897).

<sup>(3)</sup> *J. Am. Ch. Soc.*, 21, 373. (1899).

**Scheelite from New Zealand. Hardin.**

	Reduction Series Atomic Weight	Oxidation Series Atomic Weight
(1)	183.83	183.83
(2)	183.80	183.75
(3)	183.67	184.13
(4)	183.56	183.90
(5)	183.72	183.82
(6)	183.71	184.20
(7)	183.80	. . .
(8)	183.87	. . .
	<hr/>	<hr/>
Mean	183.74	183.94

The difference between the mean of the two series is 0.19. The quantities of material used, varied from two to four and a half grams. To quote Hardin concerning these results:

“Considering the number of experiments, this is the most concordant series of results ever obtained by reducing the trioxide of tungsten and weighing the resulting metal.”

**Scheelite from Bohemia. Thomas and Hardin.**

	Reduction Series Atomic Weight	Oxidation Series Atomic Weight
	183.89	184.17
	183.63	184.08
	<hr/>	<hr/>
Mean	183.76	184.12

The difference between the mean of these two short series is 0.36. Some Scheelite contains iron, and this may account for the greater difference from the preceding series.

Hardin's determinations with Wolframite material, show generally a difference of nearly a whole unit. Concerning this discrepancy he says: “Almost every series of results on the atomic mass of tungsten obtained by the reduction

of the trioxide in a current of hydrogen, and by the reoxidation of the resulting metal shows a variation between the maximum and minimum results of from one to two units, and in exceptional cases the deviation is much greater." "It seems that the results from oxidations are invariably higher than those obtained by reduction."

To Hardin's results obtained from the metal which had been prepared from the second reduction of the oxide, this difference for some reason is not so marked. His results would indicate (since the second reduction value is higher than the first), that the oxide prepared in this way, had not reached its maximum oxidation. Undoubtedly through repeated reductions and oxidations, the material will take up considerable silica, which may retard complete oxidation.

This discrepancy between the reduction and oxidation series, must be explained before any great weight can be attached to the recorded values of tungsten. To understand the effect of possible impurity, the following table is given: A molecular mixture of tungsten and the impurity, is treated as though it was all tungsten, and the resulting atomic weight calculated.

Molecular Mixture	Reduction Series Atomic Weight	Oxidation Series Atomic Weight
W+W	184.	184.
W+Mo	140.	140.
W+2Fe	148.	148.
W+3MnO	298.	298.
Loss of Material	Low	High

A consideration of these numbers, shows that: Molybdenum and iron would produce a low value; manganese a high value; volatility a low value on reduction, and a high value on oxidation. The error introduced by manganese is more than three times as costly as that introduced by iron, and more than two and a half times that introduced by



molbydenum. These ratios would apply, regardless of the proportion of the mixture.

The discrepancy between the reduction and oxidation series, can not be explained by assuming the presence of iron, manganese, or molybdenum. But loss of material would cause such a difference. Tungsten is a heavy metal and such a perceptible loss as that noted in the experiments in this paper, would certainly cause a discrepancy between the two values.

There is little difference between the reduction and oxidation series which Hardin obtained from Scheelite, and little difference between the two series given by Schneider. If loss by volatility, be advanced to explain this discrepancy, then in these series just mentioned, little volatilization could have occurred. If loss through mechanical carrying away of the material by water be advanced, then in these series the water could not have carried away much material. Hardin does not state that volatility was noticed in his Scheelite series, and Schneider states that no appreciable volatility occurred with his material. Other reasons must therefore be sought to explain this loss of material.

The specific gravity and fusibility of tungsten is such, that it seems improbable that it would volatilize in the temperature attained in a combustion furnace. It is known that alloys melt at temperatures far below the melting point of the most fusible ingredient, and the volatility would be affected in like manner. Moissan showed that the purified tungsten had a noticeably higher melting point than the impure, and that this melting point was greater than that of chromium or molybdenum. It seems quite likely that iron and molybdenum, even in traces, alloying with the tungsten would materially increase the volatility.

From these considerations it is believed, that the presence of manganese and iron, will account for the high oxidation values, for their presence would affect the result in a two



fold manner: Manganese through its inherent molecular changes  $[\text{Mn}_3\text{O}_4 \rightleftharpoons 3 \text{ MnO}]$ , and iron through its secondary action on the volatility. Further, that the presence of iron, molybdenum, manganese, and volatility, will explain the numerous discrepancies noted in the published work on this subject. Again, since iron and molybdenum decrease the value, and manganese and volatility increase the value, and iron and molybdenum influence the volatility: It is quite possible that such a mixture of these factors might occur, that the errors would be compensated. And such material, not only would give concordant reduction and oxidation values, but might even give values close to the true constant.

Viewed in this way there still remains the necessity for determinations with material from which every trace of molybdenum, iron, and manganese, together with other possible impurities, has been removed. And in all probability such material will yield values close to those obtained by Schneider, and Hardin with his Scheelite material.

The reduction and oxidation method is so simple and direct, that it will be abandoned only as a last resort. Possibly the reduction and oxidation could take place through the walls of a porous porcelain capsule, and any loss be thus prevented; the porous walls acting as a perfect filter for the aqueous vapor, and at the temperature used hydrogen or oxygen would find no difficulty in entering. Schneider has shown that the hot aqueous vapor produced in the reduction, attacks the porcelain boat and produces a slight deposit of silica on a platinum foil placed over the boat.

Schneider's material contained a trace of residue, which with the sodium carbonate test would doubtless have appeared larger. <sup>(1)</sup>Smith and Oberholtzer have shown

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<sup>(1)</sup>*J. Am. Ch. Soc.*, 15, 18. (1893).

that the previous methods usually employed for removing molybdic acid have been inadequate. In view of these considerations it seemed desirable to experiment with new methods; new methods for preparing pure material, and new methods for determining the atomic weight. In any case, the application of a new ratio will be of value.

A benzylamine tungstate has been prepared in this laboratory, which may throw some light on the subject. These organic salts may afford a means of separation and purification. A solvent may be found, suitable for molecular weight determinations. Pending the investigation of this side of the question, the following new method was tried.

The method of determining atomic weights from the loss of carbon dioxide has been applied to a number of the elements. Its application to tungsten, and the special modification of the method necessary for accurate determinations has not been before recorded. <sup>(1)</sup>Svanberg and Struve, fused molybdenum trioxide with potassium carbonate and determined the loss in weight. Their value is nearly six units too low and the method must be considered inaccurate. This method was tried with tungsten trioxide and gave values ranging from 160. to 180. The disadvantages of the method are that: The union takes place with considerable spattering; the temperature of fusion is so high that loss by volatility is probable; the alkaline carbonates when held in fusion slowly lose traces of carbon dioxide; and the resulting fusion is extremely hygroscopic.

These difficulties may be obviated by combining the oxide and sodium carbonate in aqueous solution, and then expelling the water. Operated in this manner the method possesses promising value; and has numerous advantages, among which may be mentioned that: Carbon dioxide has a molecular weight of forty-four, giving a value for com-

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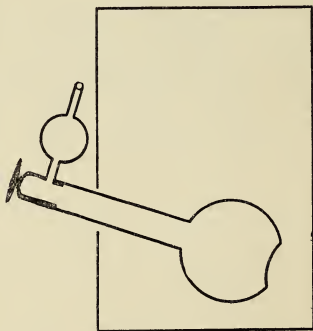
<sup>(1)</sup>*J. prakt. Ch.*, **44**, 301. (1848).

parison nearly as great as in the simple reduction and oxidation method; the union of sodium carbonate and tungsten trioxide in aqueous solution takes place at a low temperature, and the highest temperature used in the desiccator is a safe distance below the melting point of sodium carbonate, so that there is little chance for volatilization either of sodium carbonate or tungsten trioxide, and in the device used there is no chance for loss by spattering; large quantities of material may be combined with as much ease as small; the method itself would serve for a test of the purity of the material; the presence of chlorides, sulphates, sodium silicate, and potassium carbonate, would not affect the result. The presence of alkaline hydroxides would; and to prevent the possibility of this, "pure" sodium carbonate was saturated in solution with carbon dioxide, and the resulting bicarbonate heated in a vacuum at  $300^{\circ}$  for three hours.

The tungsten trioxide and sodium carbonate were combined in a glass bulb as per figure. A neutral glass is desirable for this purpose, and the bulb should be made of Jena glass, which will withstand the action of alkaline carbonates better than ordinary glass. If sodium carbonate dissolves the glass no error will be introduced, but if carbon dioxide be liberated through such solution, then the glass can not be used. To determine this point a blank experiment was made, which showed that the total weight of the bulb and sodium carbonate remained unchanged, while 0.0017 grams of glass were dissolved; hence no appreciable evolution of carbon dioxide occurred. However to prevent any possibility of such loss, a platinum bulb had better be used.

It was found that moist sodium carbonate could be heated to a constant weight, by heating for one and a half hours, at a temperature of  $300^{\circ}$  in a vacuum; and in this bulb the weight after standing several days remained unchanged.

To insure complete desiccation the bulb was always heated, double the required length of time. A water pump was used to produce the diminished pressure and since nothing can be perfectly dried in a vacuum resulting from such a pump, a calcium chloride tower was introduced. But calcium chloride will not perfectly desiccate a gas, so that phosphorus pentoxide had better be used. However, for



the preliminary experiments in hand, calcium chloride was sufficient.

The method of procedure was as follows: Some sodium carbonate was introduced in the bulb and heated for three hours at  $300^{\circ}$  in a vacuum. The suction was disconnected, and after cooling, the combined weight of bulb, sodium carbonate, and dry air was obtained. Tungsten trioxide was then introduced through a long funnel, the bulb exhausted, allowed to fill with dry air and again weighed. This gave the weight of tungsten trioxide. The weight of

the sodium carbonate further than being present in excess need not be known. Water was added and the bulb heated in a glass air bath, so that the course of the reaction could be watched. The mixture slowly effervesced, and when the action had ceased, the vacuum apparatus was attached, and the water distilled off. This water was tested and found to be neutral. The calcium chloride tower was now introduced, and the residue, consisting of a mixture of sodium tungstate and carbonate, was heated for three hours at  $300^{\circ}$  in a vacuum. After cooling and thus allowing the bulb to fill with dry air, it was detached and weighed. This loss in weight gave the carbon dioxide evolved. It may be added that the entire bulb should be inside the air bath, until the water has been removed; and then the upper portion be placed outside and the temperature increased to  $300^{\circ}$ . In this way no moisture will condense in the head, and the stopper remaining perfectly dry will not become jammed. The stopper should not be lubricated.

The following results were obtained, from impure material, which in the previous experiments in this paper gave values ranging from 182.24 to 184.82, and which was known to contain iron, manganese, and from which no effort had been made to remove molybdic acid:

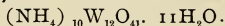
	Weight of $\text{Na}_2\text{CO}_3$ grams	Weight of $\text{WO}_3$ grams	Weight of $\text{CO}_2$ grams	Atomic Weight of Tungsten
(1)	2.7	2.0802	0.3952	183.60
(2)	2.3	2.1937	0.4173	183.30
(3)	3.5	4.0818	0.7762	183.38
(4)	3.8	3.3629	0.6394	183.41

These numbers, in that they indicate the atomic weight of tungsten, are worthless; in that they show promise for the new method, are of value. The presence of impurity would lower the result; what value the method will give for pure material can only be conjectured.

## II. THE AMMONIUM TUNGSTATES.

The ammonium tungstates are divided into two general classes, the "para salts" and the "meta salts". <sup>(1)</sup>Laurent first proposed the name "paratungstates"; and to these salts he gave the general formula  $5M_2O, 12WO_3, nH_2O$ . <sup>(2)</sup>Marignac confirmed this formula and presented numerous other types. Laurent also proposed the name "metatungstates" but they were first prepared by <sup>(3)</sup>Margueritte. Later Scheibler and Marignac worked on them and arranged them under the general formula  $M_2O, 4WO_3, nH_2O$ . From the numerous formulas proposed for the type members, these seem best established, and the salts used in the present study conformed to them.

### Solubility of Ammonium Paratungstate.



The solubility of the "para salt" as given by different workers, is as follows:

Investigator	Ratio of Salt to Water	Temperature
Anthony	1:25-28	"Cold"
Lotz	1:26.1	10.7°
"	1:33.3	"Cold"
"	1:5.8-9.6	100°
Marignac	1:22-38	15°-18°
Taylor	1:59.3	26°
"	1:69.8	21°
"	1:74.	21°
"	1:52.7	29°

### Solubility of Ammonium Metatungstate

Lotz	1:0.84	15°
Riche	1:0.35	"Ordinary"

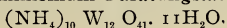
(1) *Ann. Chim. Ph.*, [3], 21, 54. (1847).

(2) *Ann. Chim. Ph.*, [3], 69, 24. (1863).

(3) *Ann. Chim. Ph.*, [3], 17, 475. (1846).

These discrepancies are irritating. The present material probably did not contain so much of the complex salt and was consequently less soluble. The solubilities of pure ammonium tungstates need to be determined and will be of value. When ammonia is passed into water containing tungstic acid, a white substance remains which has been called "paratungstate", but which is remarkably insoluble. It is far more insoluble than any ammonium paratungstate, met with in the present investigation.

### Ammonium Paratungstate.



When a solution of "para salt" is evaporated at slightly elevated temperature, monoclinic needles crystallize out; when evaporated at a boiling temperature, flat plates appear. These needles have been described as orthorhombic prisms by Kerndt, Schabus and Marignac. <sup>(1)</sup>Examined microscopically in polarized light they show an apparent parallel extinction and give a biaxial interference figure, with the acute bisectrix parallel to the long axis of the crystal; and therefore appear to be orthorhombic, but give these orthorhombic reactions on account of their remarkable twinning structure, which closely resembles the wedge shaped penetration figures seen in the hydrated Zeolites; more particularly Stilbite, which is orthorhombic in form but is a complicated monoclinic twin. It is an interesting fact that these ammoniated and hydrated crystals exhibit the same internal structure as the hydrated Zeolites.

Crops of crystals usually consist of mixtures of needles and plates in varying proportion; and many previous

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<sup>(1)</sup>I am glad to express my thanks to Professor Amos P. Brown, under whom I have had the pleasure of studying mineralogy, and who has rendered most valuable assistance in the crystallographic and microscopic study in this paper.



analyses have undoubtedly been made with such material. Such a mixture, consisting largely of needles, was digested for three days in forty times its weight of water. The water was removed and the same amount added and allowed to stand again for three days. The needles remaining contained no admixed plates. This separation does not prove that the plates are the more soluble, for they are smaller and would therefore dissolve out first. But whatever the reason for this separation, the purpose in view was accomplished; the needles were isolated. These on analysis gave the following data:

Tungsten trioxide, determined by ignition in a porcelain crucible.

"Para needles"	WO <sub>3</sub> grams	WO <sub>3</sub> per cent.
4.0016	3.4395	85.95
3.1344	2.6938	85.94

The ammonia was determined by the usual distillation and titration method.

"Para needles"	NH <sub>3</sub> grams	NH <sub>3</sub> per cent.
2.9265	0.15370	5.25
2.1002	0.10983	5.23

The water was determined as follows: The salt was covered with lead oxide, and ignited in a combustion tube in a current of dry air; the water and ammonia were caught in sulphuric acid and weighed. Subtracting from this weight the weight of the ammonia, the weight of the water was obtained.

"Para needles"	NH <sub>3</sub> + H <sub>2</sub> O grams	Water per cent.
1.2458	0.1813	9.31
1.0636	0.1536	9.20
1.5988	0.2262	8.91

These values correspond to the formula (NH<sub>4</sub>)<sub>10</sub> W<sub>12</sub> O<sub>41</sub> · 11 H<sub>2</sub>O, which requires WO<sub>3</sub>, 85.87%; NH<sub>3</sub> 5.24%; H<sub>2</sub>O



8.88%; and are also a confirmation of Marignac's formula.

When the "para needles" are crystallized from boiling water, monoclinic plates separate (Extinction parallel to diagonal of rhombic section, axial plane lying in the plane of symmetry), and to obtain these with no admixed needles, it is necessary to keep the water at the boiling point, and to remove the plates from the boiling solution as fast as they are formed. Some plates prepared in this way, gave on ignition the following per cent. of tungsten trioxide.

"Para plates"	WO <sub>3</sub> grams	WO <sub>3</sub> per cent.
0.6931	0.6170	89.02
0.2528	0.2249	88.96
0.3216	0.2860	88.93
0.5905	0.5253	88.96

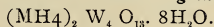
The theoretical requirement of tungsten trioxide for  $(\text{NH}_4)_{10} \text{W}_{12} \text{O}_{41} \cdot 5\text{H}_2\text{O}$ , is 88.83% and this also confirms Marignac's formula. A comparison of these two para salts is as follows:

"Para needles."  $(\text{NH}_4)_{10} \text{W}_{12} \text{O}_{41} \cdot 11\text{H}_2\text{O}$ .

"Para plates."  $(\text{NH}_4)_{10} \text{W}_{12} \text{O}_{41} \cdot 5\text{H}_2\text{O}$ .

Thus it would appear that the "para needles" in boiling water, lose six molecules of water.

### Ammonium Metatungstate.



(1) Margueritte first prepared this salt by boiling the para salts with tungstic acid. (2) Laurent prepared it, by the continued boiling of the aqueous solution of the para salts. While (3) Scheibler made it by heating the para salt to 250°, until ammonia was given off, causing a partial separation

(1) *Ann. Chim. Ph.*, [3], 17, 475. (1846).

(2) *Ann. Chim. Ph.*, [3], 21, 62. (1847).

(3) *J. prakt. Ch.*, 83, 304, (1861).

of tungstic acid, then dissolving the residue in water and allowing to crystallize. This method was adopted by <sup>(1)</sup>Persoz and later by <sup>(2)</sup>Marignac.

Scheibler describes the salt as crystallizing in large tetragonal octahedra, which effloresce in the air. If the crystals have been scratched or bruised, they quickly lose water and become opaque. Marignac observed that the crystals lose seven molecules of water at 100°, and the remaining molecule, is not driven out below 200°. Riche noticed the same behavior. When alcohol is added to a hot solution of the "meta salt", the salt  $(\text{NH}_4)_2 \text{W}_4 \text{O}_{13} \cdot 6\text{H}_2\text{O}$  separates, and according to Marignac, loses five molecules of water at 100°.

In the present investigation the "meta salt" was prepared by boiling an aqueous solution of the "para salt" for two or three days, evaporating to small bulk and allowing the sirupy liquid thus obtained to stand. Large transparent tetragonal octahedra, were obtained. After three or four recrystallizations, the crystals became almost colorless, but the yellow tint was difficult to remove. Boiled with purified bone black the greater part of the original brown color may be removed. The crystals have a high index of refraction, as also the solution. These crystals of "meta salt" were also prepared by heating the "para needles" at 150°, for four hours.

On analysis the salt gave 3.05 per cent. of ammonia.

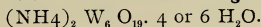
"Meta Salt"	$\text{NH}_3$	$\text{NH}_3$
grams	grams	Per cent.
0.5016	0.01531	3.05

This corresponds to  $(\text{NH}_4)_2 \text{W}_4 \text{O}_{13} \cdot 8\text{H}_2\text{O}$ , which contains 3.02% of ammonia, confirming Scheibler's formula. The characteristic physical properties were in such accord with the published data, that further analysis was not undertaken.

<sup>(1)</sup>*Ann. Chim. Ph.*, [4], 1, 101. (1864).

<sup>(2)</sup>*Ann. Chim. Ph.*, [4], 3, 72. (1864).

### Colloidal Ammonium Tungstate.



On repeating the method of Scheibler to obtain the "meta salt" (i. e. heating the "para needles" to  $250^\circ$ ), a colloidal "gum" was obtained. As many as twenty experiments failed to substantiate his claims, however, at  $150^\circ$  the "meta salt" was produced. This "gum" would dry hard and transparent and had a high index of refraction. It did not cement itself to porcelain, in the way "colloidal tungstic acid" is said to, but would shrink away from the sides of the containing vessel, and could easily be removed. Under the microscope "para needles" were found imbedded in it, and these could be removed by dialysis. The fraction passing through the parchment paper in a few hours, would crystallize in tetragonal octahedra; later fractions in "para needles", and still later fractions would not crystallize at all but consisted largely of "gum" which had passed through. This "gum" therefore when first prepared, consists of a mixture of "para salt", "meta salt", and a "colloidal salt."

The best condition for getting a large yield of the "gum" is as follows: Pulverized "para needles" are spread out on a watch glass, and heated in an air bath at  $220^\circ$  for one hour. The air bath must allow the escape of water and ammonia. The product is covered with water and boiled vigorously for fifteen or twenty minutes, when a clear (but darkened) heavy liquid results. This is filtered away from any residue and on evaporation dries into the "gum" with an almost quantitative yield. On standing several days in water, the residue will pass into the "gum" without previous boiling. At higher temperatures considerable tungstic acid is separated and the yield not so good. The "meta" salt free from "para" must be heated to  $250^\circ$ , before yielding the "gum", and the yields are nothing like so large, as by starting with the "para salts."

A marked darkening of the original white salt is noticed after heating. Different fractions of the "para salts" yield the "gum" with different degrees of readiness. These facts point to the presence of some impurity which may affect the transformations.

After dialyzing a portion of the "gum" for six days it gave the following analysis:

"Gum"	WO <sub>3</sub>	WO <sub>3</sub>
grams	grams	Per cent.
0.6150	0.5447	88.57
"Gum"	NH <sub>3</sub>	NH <sub>3</sub>
grams	grams	Per cent.
0.4825	0.01279	2.65
1.3776	0.03848	2.79

Another sample was dialyzed for thirteen days, through parchment paper, using ten changes of water of two and one-half liters each. The dialyzer had a diameter of fifteen centimeters. After four or five days, the increase of volume in the inner vessel ceased. The resulting colloidal salt, when dried on the water bath and allowed to stand in the air, slowly increased in weight. But when dried at the ordinary temperature and allowed to stand, it decreased in weight. A portion of the "colloidal salt" dried on the water bath, gave the following analysis:

"Colloidal Salt"	WO <sub>3</sub>	WO <sub>3</sub>
grams	grams	Per cent.
0.4469	0.4089	91.49
0.4523	0.4143	91.60
"Colloidal Salt"	NH <sub>3</sub>	NH <sub>3</sub>
grams	grams	Per cent.
0.6334	0.01520	2.40
0.5985	0.01415	2.36

These results point to the formula  $(\text{NH}_4)_2 \text{W}_6 \text{O}_{19} \cdot 4\text{H}_2\text{O}$ , which requires ammonia 2.24% and tungsten trioxide 91.82%.

In the same way another portion of "gum" was dialyzed for fourteen days, using nearly double the amount of water previously used. (Twelve changes of water of three and a half liters each). The resulting "colloidal salt" dried at the ordinary temperature gave the following analysis:

"Colloidal Salt"	WO <sub>3</sub>	WO <sub>3</sub>
grams	grams	Per cent.
0.1227	0.1101	89.73
0.2100	0.1885	89.76
"Colloidal Salt"	NH <sub>3</sub>	NH <sub>3</sub>
grams	grams	Per cent.
0.9243	0.01996	2.16
1.0301	0.02184	2.12

These percentages are close to the formula (NH<sub>4</sub>)<sub>2</sub> W<sub>6</sub> O<sub>19</sub> · 6H<sub>2</sub>O, which requires ammonia 2.29%, and tungsten trioxide 89.69%. This sample was dried at the ordinary temperature, the previous one at 100°. Since the salt loses weight on standing, it is likely that the additional water is not such a definite number of molecules as these analyses would indicate.

To compare the percentage of ammonia, in the different salts, the following table is given:

Salt	NH <sub>3</sub> Per cent.
"Para needles"	5.24
"Para plates"	5.42
"Meta salt"	3.02
"Colloidal Salt", (dialyzed 6 days)	2.72
" " ( " 13 " )	2.38
" " ( " 14 " )	2.14

The dialyzed salt dries hard and clear like glass, with a yellowish tint, contains no embedded crystals, and under no conditions could it be made to crystallize. It has a high index of refraction and is mixable with water in nearly all proportions. It may prove of value as a mounting medium in microscopic work, and also for the mechanical separation of minerals.

The solution has an acid reaction and absorbs ammonia with avidity. One long series of dialyzation was spoiled, by working with ammonia in the same room, the "colloidal salt" changing to the "meta" and "para" salts. By treating the solution of the "colloidal salt" with tenth-normal ammonia, till the acidity is barely neutralized, it passes into the "meta salt". Unless care is used considerable amounts of the "para salts" will be formed.

Under certain conditions the "colloidal salt" passes into a white modification, which on microscopical examination proved to be an emulsion, the globules closely resembling fat globules. On drying the white emulsion would gradually pass into the transparent variety. The emulsion can be produced by cooling a clear concentrated solution, with ice water. Oftentimes a more dilute solution, would be filled with spurious clouds, floating in suspension, and which appeared to be some foreign matter. This could not be filtered out and was a source of annoyance, until it was examined microscopically, and found to be the emulsion. Emulsions are common enough among organic substances, but are rarely observed with inorganic salts.

At first it was thought that this "colloidal salt" might be "colloidal tungstic acid", but since after prolonged dialysis, the ammonia could not be removed, it appears to be a colloidal ammonium tungstate.

The history of "colloidal tungstic acid" is of some interest. <sup>(1)</sup>Graham in 1864, reported the existence of "colloidal tungstic acid", which he prepared by treating a five per cent. sodium para tungstate solution with dilute hydrochloric acid and dialyzing the mixture. The resulting heavy liquid had a specific gravity, such that glass would float on it. <sup>(2)</sup>Sabanejeff made a molecular weight

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<sup>(1)</sup>*Proc. Roy. Soc., London*, **13**, 340. (1864).

<sup>(2)</sup>*J. Russian Ch. Soc.*, **21**, 1. (1889).

determination using cryoscopic methods, and reported the structure  $3\text{WO}_3 \cdot \text{H}_2\text{O}$ . <sup>(1)</sup> Later he retracted his determinations, and published an article on the "Non-existence of colloidal tungstic acid," saying that he had previously taken Graham's word for the composition of the "gum". On examination he found it was impossible to dialyze out the sodium, and concluded that it was amorphous sodium metatungstate. His proof of this is open to criticism, for; he states that the salt had a marked acid reaction; his analyses do not conform closely to the theoretical for sodium metatungstate; and the periods of dialysis used were not long enough to thoroughly separate the material. The conversion of one form into the other was rather violent. Sabanejeff changed the amorphous salt into the crystallized variety, by heating to  $130^\circ\text{--}150^\circ$ , in a sealed tube with an excess of water. This temperature is about the same as that which changes the ammonium "para salt" to the "meta salt" and seems altogether too high to prove the dimorphism, of the two sodium salts. Had the acidity of his colloidal salt been gradually neutralized with sodium bicarbonate or carbonate, the salt might have reverted to the crystallized form, and its dimorphism thus disproved. It seems probable that his dimorphous colloidal sodium metatungstate may prove to be a colloidal sodium tungstate analogous to the colloidal ammonium tungstate prepared in the present investigation.

#### Temperature at which the Ammonium Salts begin to lose Ammonia.

Some "para needles were placed in a glass U-tube immersed in an oil bath; dry air rapidly passed over them and into Nessler's solution. It was found that if the glass tube

<sup>(1)</sup> *Ztschr. anorg. Ch.* 14,354. (1897).



leading into the solution, was etched on the inner surface, a brown ring would form on the roughened surface, several minutes before the solution showed any traces of color. The moment of formation of this brown ring, was taken as the signal for the first appearance of ammonia, and the temperature of the bath noted. In this manner the "para needles" began to lose ammonia at  $60^{\circ}$ . The "para plates" at the same temperature, and the "meta salt" at  $120^{\circ}$ .

It is significant that the "meta salt" should begin to lose ammonia at  $120^{\circ}$ ; it was prepared at  $150^{\circ}$ . It seems improbable that a salt which begins to lose ammonia at  $120^{\circ}$  could be prepared at  $250^{\circ}$ , as recorded by Scheibler.

Marignac and others dry the "para salts" at  $100^{\circ}$  and attribute the loss to expulsion of water, but a part of that loss is ammonia. However, the ammonia that escapes below  $100^{\circ}$  is but a trace.

### Action of Dry Ammonia Gas on "Para Needles".

The effect of ammonia on "para needles" was determined as follows: A boat of needles was placed in a bent tube immersed in paraffin. Ammonia gas (dried by lime and caustic potash) was passed over it, and escaped through 0.75 cm. mercury and 9.00 cm. of water, so that the gas was under a pressure of about fourteen millimeters of mercury, in excess of the atmospheric pressure. After heating for one and a half hours the boat was placed in a capsule and weighed. The percentage of ammonia was then determined. The loss in weight, together with the percentage of ammonia furnish data, from which the changes in the salt may be calculated.



# Action of Dry Ammonia Gas on Ammonium Paratungstate.

Temper- ature	Para Needles" grams	Weight after treatment	NH <sub>3</sub> grams	Molecules of NH <sub>3</sub> added	Molecules of water lost	Approximate formula
			Original	"para needles."		
100°	0.7193	0.6904	0.04276	+1.3	— 8.5	10NH <sub>3</sub> . 12WO <sub>3</sub> . 16H <sub>2</sub> O
110°	1.0012	0.9632	0.06295	+2.0	— 8.7	11NH <sub>3</sub> . 12WO <sub>3</sub> . 7H <sub>2</sub> O
120°	1.1203	1.0796	0.07268	+2.4	— 8.8	12NH <sub>3</sub> . 12WO <sub>3</sub> . 7H <sub>2</sub> O
130°	0.9936	0.9619	0.06901	+3.2	— 8.8	12NH <sub>3</sub> . 12WO <sub>3</sub> . 7H <sub>2</sub> O
140°	0.8391	0.8101	0.05563	+2.7	— 8.7	13NH <sub>3</sub> . 12WO <sub>3</sub> . 7H <sub>2</sub> O
150°	1.2278	1.1768	0.07514	+1.7	— 9.1	13NH <sub>3</sub> . 12WO <sub>3</sub> . 7H <sub>2</sub> O
160°	1.2204	1.1696	0.06530	+0.2	— 7.7	12NH <sub>3</sub> . 12WO <sub>3</sub> . 8H <sub>2</sub> O
200°	0.9730	0.9251	0.04797	—0.6	— 8.3	10NH <sub>3</sub> . 12WO <sub>3</sub> . 8H <sub>2</sub> O
250°	1.3238	1.2286	0.05872	—1.6	—11.5	9NH <sub>3</sub> . 12WO <sub>3</sub> . 8H <sub>2</sub> O

*Attention is directed to the nearly constant loss of water; and that at 130° the maximum amount of ammonia is absorbed. At 250° tungsten trioxide was separated.*

These ammonio-addition salts are quite unstable; when dissolved in water, the water is made alkaline and "para needles" crystallize out; when allowed to stand in the air they revert to their original weight, and percentage of ammonia, as evidenced in the following experiments: Two boats of "para needles" placed side by side in the same U-tube were heated together in dry ammonia gas at 130° for one and a half hours. The ammonia in one was determined at once; the companion boat was allowed to stand over night, before determining the ammonia.

	"Para needles"	NH <sub>3</sub>	NH <sub>3</sub>
	grams	grams	Per cent.
Boat A.	0.8754	0.06242	7.13
Companion Boat A.	0.9718	0.05034	5.18
Boat B.	0.8744	0.05859	6.70
Companion Boat B.	0.9321	0.04866	5.22

Companion Boat B, after standing over night, weighed 0.9319 grams. It appears therefore that the salt has lost its added ammonia, and absorbed its lost water.

### **Action of Moist Ammonia Gas on the "Meta Salt" at the Ordinary Temperature.**

A boat containing 0.9874 grams of "meta salt" was placed in a vacuum desiccator, over ammonium hydroxide. After standing several hours the transparent crystals were found to be replaced, by a white salt covered with water. This water was removed by spontaneous evaporation in the air, and the residue weighed 0.9327 grams and contained 0.04803 grams ammonia, equivalent to 5.15%, or 3.83 molecules of ammonia added. Hence the "meta salt" has been

changed by moist ammonia gas, at the ordinary temperature into the "para needles", and the conversion has been practically quantitative.

The "para needles" being a hundred times more insoluble than the "meta salt", have crystallized out from the water of crystallization of the latter. In other words the water of the old salt has been pushed out by the new salt, and the new salt is found "swimming" in the water of crystallization of the old salt. On several days standing the amount of water in the boat gradually increased, so that water evidently slowly distills into the boat.

#### **Action of Moist Ammonia Gas on the "Meta Salt" at 100°.**

"Meta salt" treated with ammonia passes to the "para needles," and a solution of these at 100° changes to the "para plates"; so that the action of moist ammonia on the "meta salt" at 100° can almost be predicted. A boat containing 0.4408 grams "meta salt" (placed in the same apparatus used for determining the action of dry ammonia on the "para needles"), was treated with moist ammonia gas at 100°, for one hour. After treatment the salt weighed 0.4189 grams; after standing sixty hours in the air it weighed 0.4186 grams. This contained 0.02276 grams of ammonia equivalent to 5.44%, or 4.04 molecules of added ammonia. Hence at 100° moist ammonia gas transforms the "meta salt" into the "para plates." Dry ammonia gas would probably form the ammonio-addition product produced at that temperature.

## THEORETICAL CONSIDERATIONS.

## Normal Ammonium Tungstate.

The normal sulpho-salt  $(\text{NH})_2\text{WS}_4$  exists and one might expect the existence of the corresponding oxygen salt. However, normal ammonium tungstate has never been prepared. <sup>(1)</sup>Marignac by the spontaneous evaporation of a solution of "para salt", in a bell jar over lime (which would absorb water and not ammonia), obtained a salt of the composition  $2(\text{NH}_4)_2\text{O} \cdot 3\text{WO}_3 \cdot 3\text{H}_2\text{O}$ . This salt was soluble in cold water but soon changed to the "para salt." In the air it gave off ammonia reverting to the "para salt."

Various methods have been suggested in the present work, to make the normal salt. Among which may be mentioned the following:

1. Pass ammonia into a solution of the "meta salt" cooled to zero degrees.
2. Pass ammonia into the "colloidal salt" cooled to zero degrees.
3. Pass ammonia into benzene (or some other liquid not mixable with water) in which is suspended the ammonium salt.
4. Action of liquid ammonia on tungstic acid.

Of these methods the first only was tried, a crystallized salt obtained which in the air lost ammonia, but it was not analyzed.

The ratio between the ammonia and tungsten trioxide, in the different salts is tabulated as follows:

Salt	$\text{NH}_3$	:	$\text{WO}_3$
Theoretical Normal Salt	1.0	:	0.5
Marignac's Salt (unstable)	1.0	:	0.75
"Meta Salt"	1.0	:	2.0
"Para Salt"	1.0	:	1.2

<sup>(1)</sup>*Ann. Chim. Ph.*, [3], 69, 22. (1863).

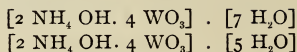
From these ratios it is seen that Marignac's salt is the closest to the normal ratio that has yet been prepared, but it was not stable at the ordinary temperature. Of the other salts, the "para salt" is the closest to the normal ratio. The para ammonio-addition salts prepared in this investigation are unstable, easily losing their excess of ammonia. It seems therefore that at the ordinary temperature, tungsten can not hold any more ammonia than that expressed by the para ratio. It is believed that the formation and preservation of the normal salt is simply a question of temperature.

### Water of Crystallization.

In boiling water the "para needles" lose exactly six molecules of water and crystallize out as "para plates." Five molecules of water remain in the salt, and it is significant that five ammonium oxide molecules remain also. Possibly five ammonium oxide influence five water in such a manner, that these molecules are more firmly bound or linked than the others. Whatever explanation may be advanced, the fact remains that six molecules of water are driven out at  $100^{\circ}$ , and five are not.

The "meta salt",  $(\text{NH}_4)_2\text{W}_4\text{O}_{13} \cdot 8\text{H}_2\text{O}$ , at  $100^{\circ}$  loses seven molecules of water. The remaining molecule can not be driven out, below  $200^{\circ}$ . "The "meta salt" from alcohol  $(\text{NH}_4)_2\text{W}_4\text{O}_{13} \cdot 6\text{H}_2\text{O}$ , at  $100^{\circ}$  loses five molecules of water, and the remaining molecule behaves as before. In these salts one molecule of water must be very differently combined from the others, for one requires  $200^{\circ}$  of temperature to remove it, while the others leave the salt quite rapidly even at the ordinary temperature. The number of water molecules remaining, again correspond to the number of ammonium oxide molecules, and the probability increased that one ammonium oxide influences one hydrogen oxide.

These two salts may be written:



At  $100^\circ$  in the air the water is split off from both salts, and the common residue or nucleus  $[2 \text{ NH}_4 \text{ OH. } 4 \text{ WO}_3]$  remains, which is stable up to  $200^\circ$ .

### Ammonia Content.

The para "needles" and "plates" begin to lose ammonia at  $60^\circ$ ; the "meta salt" at  $120^\circ$ . If the ammonia in these salts is combined in the same manner, it ought to be given off at the same temperature. Such is not the case, and consequently it looks as though part of the ammonia was differently combined or linked than the rest. At  $150^\circ$  the "para salts" lose four molecules of ammonia, and revert to the "meta salt." The "meta salt" on the addition of four molecules of ammonia advances to the "para salt". The commonest double salt of sodium with ammonium paratungstate, has the composition  $\text{Na}_4 (\text{NH}_4)_6 \text{W}_{12} \text{O}_{41} \cdot 15 \text{H}_2\text{O}$  (Knorre, Marignac, Hallopeau.) Four molecules of ammonia have been replaced by four molecules of sodium. The fact that all the ammonia has not been displaced by sodium, indicates that four molecules are differently combined than the others, and probably these are the same four which are lost at  $150^\circ$ , (or on long standing in water, even at the ordinary temperature.)

### Transformations.

The transformations in this series of salts, are of interest. The entire series may be prepared from the first member, or the entire series may be prepared from the last member. In fact, the whole series may be prepared from any member.

Temperature of formation.	Series		
(Below 100°)	"Para needles"	$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$	$11\text{H}_2\text{O}$
(100°)	"Para plates"	$(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$	$5\text{H}_2\text{O}$
(150°)	"Meta salt"	$(\text{NH}_4)_2\text{W}_4\text{O}_{13}$	$8\text{H}_2\text{O}$
(220°)	"Colloidal salt"	$(\text{NH}_4)_2\text{W}_6\text{O}_{19}$	$4\text{ or }6\text{H}_2\text{O}$

Before taking up the transformations, attention is called to the difference between the last two salts. This difference is  $2\text{WO}_3 \cdot 2\text{ or }4\text{H}_2\text{O}$ . <sup>(1)</sup>Gibbs in his classic work, on the complex inorganic acids, pointed out the existence of a "homologous series" of metatungstates having a common difference  $2\text{WO}_3 \cdot \text{RO}$ . The difference noticed here, while not exactly the common difference discovered by him, is equivalent to it, as far as the tungsten trioxide is concerned.

The two "para salts" (in the series) on long standing in solution, at the ordinary temperature revert to the "meta salt". The "colloidal salt" on absorbing ammonia, reverts to the "meta salt". The "meta salt" on standing reverts to the residue  $[2\text{NH}_4\text{OH} \cdot 4\text{WO}_3]$ . This residue, therefore may be considered a decomposition product or nucleus of the whole series. It is the most stable portion in the entire series; when it is attacked, the structure of the salt is broken down, and tungstic acid separated. It is well known that the "meta salts" are broken down by acids or alkalies only with difficulty.

Beginning with the first member, we may go down the series, by physical means: "Para needles" heated to 100° (in water) go the "para plates". The "plates" at 150° (in air) pass into the "meta salt". The latter heated to 250° changes to the "colloidal salt."

Again, we may proceed down the series by chemical means. "Para needles" treated with acetic acid go to

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<sup>(1)</sup>*Proc. Am. As. Adv. Sci.*, 47, 1, (1898) and previous papers.

the <sup>(1)</sup>“para plates”. The “para plates” boiled with tungstic acid or dilute mineral acids pass into the “meta salt”. The “meta salt” as yet has not been changed into the “colloidal salt” by chemical means; boiling with tungstic acid did not produce it.

To reverse the transformations: Beginning with the last member we may proceed up the series, by chemical means. The acidity of the “colloidal salt” neutralized with ammonia, produces the “meta salt”. The “meta salt” on the addition of four molecules of ammonia at 100°, advances to the “para plates”. The “para plates” on the addition of water at the ordinary temperature proceed to the “para needles”.

From these considerations it appears probable, that a common nucleus runs through the whole series, and that the nucleus is  $[2\text{NH}_4\text{OH} \cdot 4\text{WO}_3]$ . The molecular weight of this nucleus is, as yet unknown, it may be a polymer, or it may be one-half, which would correspond to Gibbs' difference  $[\text{RO} \cdot 2\text{WO}_3]$ , and might be written  $\left\{ \frac{\text{NH}_4}{\text{H}} > \text{O} \cdot 2\text{WO}_3 \right\}$ . The simplest view of the matter would favor the nucleus  $[\text{NH}_4 \text{OH} \cdot 2\text{WO}_3]$ , and until molecular weight determinations have been made the salts may be written with this in mind.

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<sup>(1)</sup> *Gibbs Am. Ch. J.*, 1, 229. (1879).

Gibbs states that the salt formed with acetic acid has the composition  $(\text{NH}_4)_{10} \text{W}_{12} \text{O}_{41} \cdot 6\text{H}_2\text{O}$ , and adds that it appears to be the same salt, to which Marignac attributed  $5\text{H}_2\text{O}$ . The temperature of crystallization may clear up the discrepancy.



# AMMONIUM, "PARA" AND "META" TUNGSTATES.

## Temperature of formation

(Below 100°)	"Para needles"	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 4[\text{NH}_4\text{OH}] \cdot 6[\text{H}_2\text{O}]$
(100°)	"Para plates"	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 4[\text{NH}_4\text{OH}]$
(150°)	"Meta salt"	$2[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 7[\text{H}_2\text{O}]$
(220°)	"Colloidal salt"	$2[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 2[\text{WO}_3] \cdot 3 \text{ or } 5[\text{H}_2\text{O}]$

## PARA AMMONIO-ADDITION PRODUCTS.

### In Ammonia Gas

(100°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 4[\text{NH}_3]$
(110°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 5[\text{NH}_3]$
(120°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 5[\text{NH}_3]$
(130°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 6[\text{NH}_3]$
(140°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 6[\text{NH}_3]$
(150°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot [\text{NH}_4\text{OH}] \cdot 5[\text{NH}_3]$
(160°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 2[\text{NH}_4\text{OH}] \cdot 2[\text{NH}_3]$
(200°)	$6[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 2[\text{NH}_4\text{OH}] \cdot [\text{NH}_3]$
(250°)	$4[\text{NH}_4\text{OH} \cdot 2\text{WO}_3] \cdot 4[\text{WO}_3] \cdot 4[\text{NH}_3]$

## PARA AMMONIO-SUBSTITUTION SALT.



These tables suggest the presence of "nuclei" and "side-chains". The "para salts" appear to be polymers of the "meta salts", linked together by, or to which are added, the "side-chains". The "side-chains" may be split off by physical or chemical means, and substitutions appear to take place in them. Where transformations require the splitting off of part of the structure, both physical and chemical means may be employed to accomplish the desired end. But where transformations demand the addition of these parts, then chemical means only can accomplish the purpose.

(<sup>1</sup>)Smith and Hardin have demonstrated the tendency of tungsten trioxide itself, to polymerize. And after such polymerization the material is insoluble in sulphur monochloride, whereas before, it is soluble. The polymerized ammonium salts in this series, are over a hundred times more insoluble than the unpolymerized.

It is significant, that the temperature which breaks down the "para salt" into the "meta salt" (i. e.  $150^{\circ}$ ), is not far from that temperature ( $130^{\circ}$ ), at which the "para salt" in ammonia gas, is able to take on the maximum amount of ammonia. In other words, the polymer absorbs the most ammonia at a temperature near its rupture temperature. It looks as though the polymer when "opened up" was enabled to "take in" more ammonia.

There is no reason why the compounds of carbon, should have a monopoly over, "homologous series", "polymerizations" "ring formations", "side-chains", "substitution products" or "gums".

Organic "gums" are supposed to be high polymers of some simple form, and the polymerization is usually accompanied with insolubility and non-crystalline character. The "gum" in the present investigation appears to be an ammo-

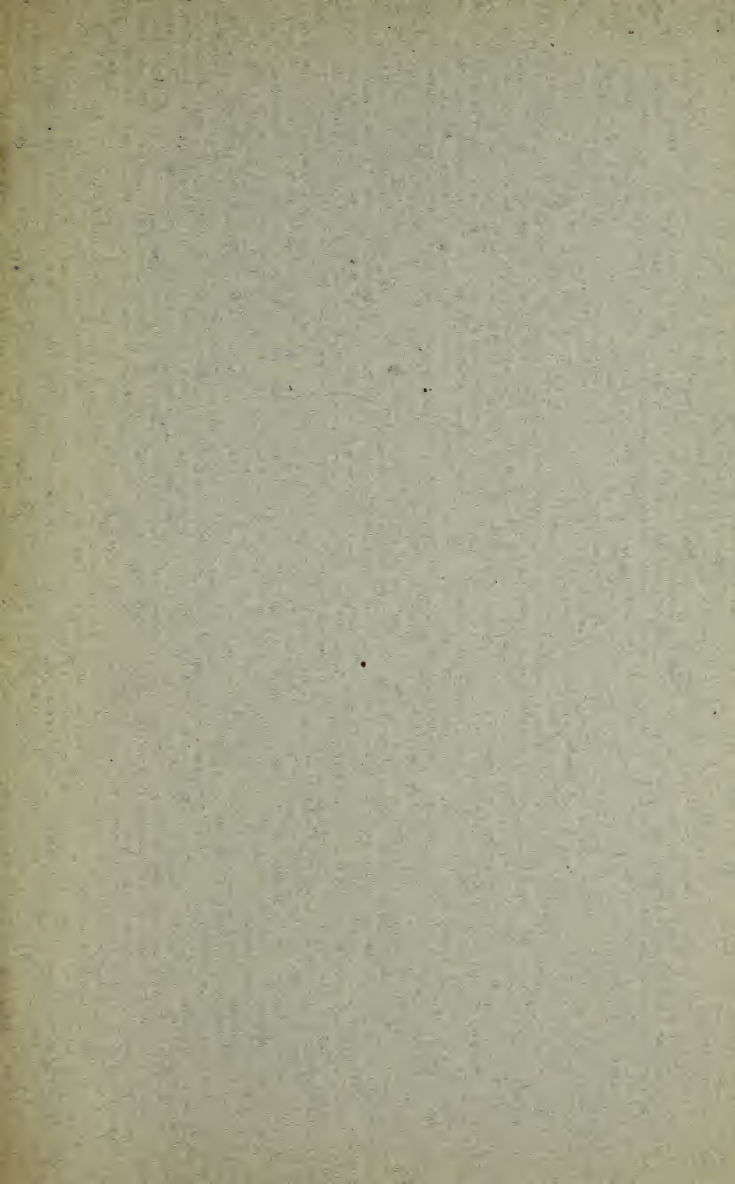
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(<sup>1</sup>)*J. Am. Ch. Soc.*, 21, 1007. (1899).

mium salt, but no surprise will be expressed, if it proves to be an acid salt of "colloidal tungstic acid" and ammonium metatungstate. If "colloidal tungstic acid" exists, it would probably be a polymer of tungsten trioxide, and its affinity for ammonia would be so great that only with difficulty could the two be separated. In one experiment, a long process of dialyzation was ruined by the presence of ammonia in the atmosphere of the room; and who knows how much ammonia the other experiments absorbed. Traces of ammonia would neutralize the work performed by days of dialyzation. The subject needs to be further investigated.

It is hoped that benzylamine tungstate will form a similar series of salts, and yielding more readily to organic methods, facts concerning their molecular magnitude and constitution may be developed.

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